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Working up of reaction discharges from phosgenation reactors

The present invention relates to a process for the preparation of
5 isocyanates by reacting primary amines with phosgene in a
reactor, the reaction discharge being present in the form of a
suspension which contains the isocyanate to be prepared, as a
liquid, and carbamyl chlorides as a solid, and working up the
suspension in a film evaporator, and a production plant for
10 carrying out this process.

Numerous processes for the preparation of isocyanates by reacting
primary amines with phosgene are known. For example, US 3,140,305
describes a process for the preparation of substantially pure
15 aromatic diisocyanate by reaction of amines with phosgene and
subsequent distillation of the reaction products.

It is furthermore known that the use of a large excess of
phosgene relative to the amino groups used leads to high
20 selectivities with respect to the isocyanate prepared and may
thus have a decisive effect on the cost-efficiency of the
process. However, the phosgene hold-up of the plant increases
with increasing ratio of phosgene to amino groups, a very short
phosgene hold-up of the plant being desirable owing to the
25 toxicity of phosgene.

It is an object of the present invention to provide a process for
the preparation of isocyanates which makes it possible to carry
out the reaction with very small losses of yield in combination
30 with a very short phosgene hold-up.

We have found that this object is achieved if the reaction
discharge from the phosgenation reactor, which is present in the
form of a suspension which contains the isocyanate to be
35 prepared, as a liquid, and carbamyl chlorides as a solid is
transferred to a film evaporator for working up. The achievement
of the object was surprising for a person skilled in the art
since there have to date been considerable reservations against
the use of solids in film evaporators, in particular in thin-film
40 evaporators.

The present invention relates to a process for the preparation of
isocyanates by reacting primary amines with phosgene in a
reactor, the reaction discharge being present in the form of a
45 suspension which contains the isocyanate to be prepared, as a
liquid, and carbamyl chlorides as a solid, wherein the suspension
is worked up in a film evaporator.

The present invention furthermore relates to the use of film
evaporators for working up reaction discharges from phosgenation
reactors, the reaction discharges being present in the form of a
suspension which contains the isocyanate to be prepared, as a
5 liquid, and carbamyl chlorides as a solid.

Finally, the present invention relates to a production plant for
the production of isocyanates by reacting primary amines with
phosgene, comprising
10 a reactor in which the reaction of primary amines with phosgene
takes place and
at least one film evaporator to which the reaction discharge of
the reactor, which is present in the form of a suspension which
contains the isocyanate to be prepared, as a liquid, and carbamyl
15 chlorides as a solid, is fed.

Any desired primary amine or a mixture of two or more of these
amines can be used for the novel process. Aromatic amines, in
particular those of the diaminodiphenylmethane series or the
20 higher homologs thereof, are preferably used. Examples are
methylenediphenylamine (MDA; individual isomers, isomer mixture
and/or oligomers thereof), toluenediamine (TDA), n-pentylamine,
6-methyl-2-heptanamine, cyclopentylamine, R,S-1-phenylethylamine,
1-methyl-3-phenylpropylamine, 2,6-xylidine,
25 2-(N,N-dimethylamino)ethylamine,
2-(N,N-diisopropylamino)ethylamine, C11-neodiamine,
3,3'-diaminodiphenyl sulfone and 4-aminomethyl-1,8-octandiamine.
MDA and TDA are preferably used. The process can also be used for
aliphatic amines. The use for 1,6-diaminohexane and for
30 isophoronediamine is preferred here.

The novel process is accordingly suitable for the preparation of
any desired isocyanates. The process can be particularly
advantageously used for the preparation of methylene(diphenyl
35 diisocyanate) (MDI) and tolylene diisocyanate (TDI).

In the preparation of isocyanate by reacting a primary amine with
phosgene, carbamyl chlorides are formed as intermediates in a
first fast step according to the following equation, which
40 carbamyl chlorides decompose to isocyanates and HCl in a
rate-determining, slow step in an equilibrium reaction:

$$R-NH_2 + COCl_2 \rightarrow R-NH-COCl + HCl \Leftrightarrow R-NCO + 2\ HCl,$$
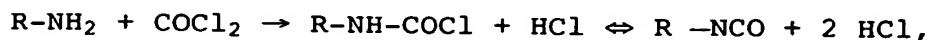
45 where R is an organic radical.

Furthermore, the hydrogen chloride formed can react with amines
to give amine hydrochlorides $(R-NH_3^+Cl^-)$.

The reaction of phosgene with diamine is carried out in the novel
5 process in a reactor. This may be any conventional reactor which
is known from the prior art and is suitable for phosgenation,
preferably for continuous phosgenation, and withstands the
customary pressures. Suitable materials are, for example, metals,
such as steel, silver or copper, glass, ceramic or homogeneous or
10 heterogeneous mixtures thereof. Steel reactors are preferably
used.

The reactor designs known from the prior art can generally be
used. Tubular reactors, columns and stirred kettles are
15 preferably used.

In the novel process, the mixing of the reactants (amine and
phosgene) is carried out in a mixing apparatus which permits high
shearing of the reaction stream passed through the mixing
20 apparatus. A preferably used mixing apparatus is a rotation
mixing apparatus, a mixing pump or a mixing nozzle, which is
located upstream of the reactor. A mixing nozzle is particularly
preferably used.

25 The novel process comprises continuous, semicontinuous and
batchwise processes. Continuous processes are preferred.

The reaction of amine with phosgene can be carried out in the
liquid phase or in the gas phase. The reaction conditions, for
30 example pressure and temperature, are generally parameters known
from the prior art.

The novel process is preferably carried out in the liquid phase.

35 In a reaction of amine with phosgene in the liquid phase, an
inert solvent can be added to the novel process. This inert
solvent is usually an organic solvent or a mixture thereof.
Chlorobenzene, dichlorobenzene, trichlorobenzene, toluene,
hexane, diethyl isophthalate (DEIP), tetrahydrofuran (THF),
40 dimethylformamide (DMF), benzene and mixtures thereof are
preferred. Chlorobenzene is particularly preferred. The inert
solvent can preferably be added to the amine at the beginning of
the reaction. The inert solvent is usually used in an amount of
from 5 to 1 000, preferably from 50 to 500, % by weight, based on
45 the amount of amine used.

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The reaction mixture emerging from the reactor (reaction discharge) is present in the form of a suspension. The suspension contains the isocyanate to be prepared, as a liquid, and still undecomposed carbamyl chlorides as solids. The suspension
5 emerging from the reactor may furthermore contain amine hydrochlorides and/or ureas (R-NH-CO-NH-R) as solids.

Usually, carbamyl chlorides are present in an amount of from 0.01 to 35, preferably from 0.02 to 30, % by weight, based on the
10 amount of the isocyanate to be prepared, in the suspension (reaction discharge). The carbamyl chloride is generally present in an amount of from 5 to 35, preferably from 15 to 30, % by weight, based on the amount of the isocyanate to be prepared, in the preparation of MDI. In the preparation of TDI, the carbamyl
15 chloride is generally present in an amount of from 0.01 to 30, preferably from 0.02 to 20, % by weight, based on the amount of the isocyanate to be prepared.

Furthermore, amine hydrochlorides are generally present in an
20 amount of from 0.01 to 10, preferably from 0.1 to 5, particularly preferably from 0.5 to 3, % by weight, based on the amount of the isocyanate to be prepared, in the suspension (reaction discharge).

25 Finally, ureas are generally present in an amount of from 0.05 to 15, preferably from 0.5 to 10, particularly preferably from 1 to 5, % by weight, based on the amount of the isocyanate to be prepared, in the suspension (reaction discharge).

30 In the context of this invention, film evaporators are understood as meaning all apparatuses in which the liquid phase of the medium to be vaporized is applied as a film (the film evaporator then corresponds to a thin-film evaporator) over the heating surface and is transported along said surface without backmixing
35 for the purpose of vaporization. The film is bounded on one side by the heating surface and on the other side by the gaseous phase. The falling-film evaporator and the thin-film evaporator are examples of film evaporators.

40 Usually, the liquid or suspension to be vaporized in the film evaporator has a film thickness of from 0.01 to 10 mm, preferably from 0.1 to 6 mm, particularly preferably from 0.5 to 3 mm.

In a possible embodiment, the film evaporators used may be
45 thin-film evaporators. Thin-film evaporators are known in the prior art and are described, for example, in Ullmanns Enzyklopädie. In general, thin-film evaporators serve for

vaporizing thermally sensitive substances from high-boiling
residues and for concentrating thermally labile substances, a
liquid being applied as thin films to heated surfaces by allowing
it to trickle down or by the action of centrifugal force, wipers
5 or the like.

Examples of suitable thin-film evaporators are apparatuses in
which the liquid film is produced mechanically, for example
SAMBAY and LUWA thin-film evaporators and Sako thin-film
10 evaporators and ALFA-LAVAL centritherm evaporators.

In a preferred embodiment, film evaporators which have no moving
parts are used. Examples of these are falling-film evaporators
(also referred to as downflow evaporators) and helical tube
15 evaporators.

In this invention, the film evaporators used are preferably
falling-film evaporators. The heat transfer surface may be in the
form of tubes or plates. Cylindrical tubes are preferably used.
20

The film evaporator used in the novel process, preferably the
falling-film evaporator used, is usually operated at from
0.5 mbar to 25 bar, preferably from 0.5 to 20, particularly
preferably from 1 to 18, bar.
25

If the isocyanate to be prepared is TDI, the film evaporator used
in the novel process, preferably the falling-film evaporator
used, is operated at from 0.5 mbar to 25 bar, preferably from 0.5
to 20, particularly preferably from 1 to 18, in particular from 2
30 to 17, bar.

If the isocyanate to be prepared is MDI, the film evaporator used
in the novel process, preferably the falling-film evaporator
used, is operated at from 0.5 mbar to 25 bar, preferably from 0.5
35 to 20, particularly preferably from 1 to 18, in particular from
1.5 to 10, bar.

The temperature in the film evaporator is usually from 30 to
300°C, preferably from 50 to 200°C.
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The residence time of the liquid to be vaporized depends on the
temperature established. Usually, the residence time in the film
evaporator is from 5 seconds to 20 minutes, preferably from 20
seconds to 10 minutes, particularly preferably from 40 to 400
45 seconds. For achieving the desired residence time, it may be
expedient to connect two or more, preferably two, film
evaporators in series. The abovementioned residence times are

then based on the sum of the residence times in the film
evaporators connected in series.

The suspension phase and the liquid phase may flow cocurrent or
5 countercurrent. Liquid and gaseous phases are preferably
transported countercurrent in the film evaporator used.

In a possible embodiment, the suspension (reaction discharge) is
worked up in two, or if required more than two, film evaporators
10 arranged in series. In a preferred embodiment, the two film
evaporators arranged in series operate at different pressure
levels.

In a preferred embodiment, two film evaporators are used, the
15 first film evaporator operating at from 0.5 to 25, preferably
from 0.5 to 20, particularly preferably from 1 to 18, bar and the
second film evaporator operating at a pressure which is from 0.01
to 1, preferably from 0.02 to 0.5, particularly preferably from
0.05 to 0.2, bar lower than the pressure of the first film
20 evaporator.

If more than two film evaporators are connected in series, the
first film evaporator operates at from 0.5 to 25, preferably from
0.5 to 20, particularly preferably from 1 to 18, bar and each
25 further film evaporator has a pressure which is in each case from
0.01 to 1, preferably from 0.05 to 0.2, bar lower than the
pressure of the preceding film evaporator.

A preferred design for the use of film evaporators in the working
30 up of reaction discharges is shown in figure 1:

Figure 1 shows two falling-film evaporator units I and II
arranged in series. In figure 1:

35 I   is the first falling-film evaporator
   II   is the second falling-film evaporator
   III   is the feed of the reactor discharge
   IV   is the removal of the gas phase
   V   is a phase separation container
40 VI   is a tube bundle with jacket heating
   VII   is the removal of the desired product (liquid)
   VIII   is a pressure reducing means
   IX   is a liquid distributor
   X   is a liquid collector
45

Falling-film evaporator I operates at > 0.5, preferably from 1 to 5, bar absolute; II operates at a pressure which is below that of I but is preferably > 3 mbar, very particularly preferably > 50 mbar.

5

The suspension-like reaction discharge is added to the top of I. Before addition to the top of I, the reaction discharge is, if required, passed again through a pressure reducing means, preferably a pressure reducing valve, and fed to a phase

10 separation container in order to reduce the pressure to the operating pressure of I. After addition to the top of I, the suspension taken from the phase separation container first enters a distributor, for example a perforated box distributor, and is distributed there over tubes of a tube bundle.

15

The tubes have an external diameter of from 10 to 200 mm, preferably from 25 to 80 mm. The length of the tubes is from 0.5 to 15 m, preferably from 3 to 9 m. The number of tubes per falling-film evaporator is usually from 10 to 10 000, preferably

20 from 100 to 1 000, tubes.

The tubes have, for example, an external diameter of 38 mm, a wall thickness of 2.3 mm and a length of 6 000 mm. For example, about 560 tubes are present. The suspension is collected at the

25 lower exit of the tubes and is fed to a further distributor. Another tube bundle follows, as stated above.

At the lower part of this tube bundle is a level regulator from which the suspension is fed via a valve to an expansion vessel

30 for pressure adaptation to II. II is designed analogously to I.

The primarily liquid suspension phase has a residence time of about 10 seconds in each unit comprising distributor and tube bundle. This results in a total residence time of about

35 4 x 10 seconds = 40 seconds. By means of surface structuring, the residence time of solids can be increased by a factor of about three relative to the purely liquid phase. This gives a maximum residence time of the units I and II together of about 2 minutes.

40 Within a residence time of 40 seconds, carbamyl chlorides can be reduced at a wall temperature of 150°C from an initial content of from 0.1 to 0.01% by weight to 1 ppm, based on the initial amount of carbamyl chloride. As a result of the surface structuring, even a reduction of from 10 - 0.1% by weight to 1 ppm is

45 possible.

The liquid phase is then fed to a further working up, which may differ depending on the isocyanate prepared. In general, the inert solvent is separated off in the next step. This can be effected in a column or once again in a film evaporator,
5 preferably a falling-film evaporator.

In a preferred embodiment, the distillation column is connected downstream of the one film evaporator used or of the plurality of film evaporators used.
10

In the film evaporators, the main cleavage of the isocyanate takes place with simultaneous phosgene separation. According to the invention, cleavage with a low phosgene hold-up is achieved by using the film evaporator. The final conversion of the
15 carbamyl chloride, which requires a relative long time, is then achieved by adding the already phosgene-poor solution to the distillation column, in which hold-up and hence residence time are adequately produced without a greater additional phosgene hold-up. The isocyanate solution is taken off at the bottom of
20 the distillation column, and the HCl formed in the remaining cleavage, and the remaining phosgene, are taken off at the top of the distillation column.

With the use of a plurality of film evaporators, the distillation
25 column is usually connected downstream of the film evaporator arranged as the last one in the process sequence.

The gas phases removed, which mainly comprise HCl and phosgene and to a lesser extent solvent and traces of the isocyanate, are
30 fed to a further working up, HCl and phosgene being separated. Any traces of isocyanate and/or solvent remain in the phosgene. The phosgene is recycled into the reaction part.

The novel process is carried out in a production plant which
35 comprises a reactor, in which the reaction of primary amines with phosgene takes place, and
at least one film evaporator to which the reaction discharge of the reactor is fed, which discharge is present in the form of a suspension which contains the isocyanate to be prepared, as a
40 liquid, and carbamyl chlorides as a solid.

In addition to reactor and film evaporator, the production plant generally furthermore comprises the reaction stages known from the prior art, for example storage containers, mixing apparatuses
45 and working-up stages.

A preferred embodiment of a novel production plant is to be explained in more detail on the basis of a general process diagram according to figure 2. In figure 2:

5 I   is a phosgene vessel
II   is an amine vessel
III   is a mixing apparatus
V   is a reactor
VI   ·is a film evaporator
10 VII   is a second working-up apparatus
VIII   is an isocyanate vessel
IX   is a phosgene working-up
X   is a solvent working-up
1   is the phosgene feed
15 2   is the amine feed
3   is the feed of inert solvent
4   is the hydrogen chloride and inert solvent separated off
5   ·is a recycled isocyanate stream (optional)
6   is the discharged hydrogen chloride
20 7   is the isocyanate separated off
8, 11   are inert solvent which has been separated off
9   is worked-up inert solvent
10   is worked-up phosgene

25 The amine from the amine vessel II and phosgene from the phosgene vessel I are mixed in a suitable mixing apparatus III. In an optional embodiment, the mixture of amine and phosgene is additionally mixed with recycled isocyanate as solvent. After the mixing, the mixture is transferred to a reactor V. Apparatuses 30 which are both mixing apparatus and reaction apparatus can also be used, for example tubular reactors having flange-connected nozzles.

Working-up apparatus VI is a film evaporator in one of the 35 embodiments described above. Usually, hydrogen chloride and any inert solvent and/or small amounts of the isocyanate stream are separated off here from the isocyanate stream.

Working-up apparatus VII is a conventional distillation unit or a 40 further film evaporator. In the second separation apparatus VII, inert solvent is preferably separated off and then worked up (X) and recycled to the amine vessel II.

In addition to the novel process and the novel production plant, 45 the present invention furthermore relates to the use of film evaporators for working up reaction discharges from phosgenation reactors, the reaction discharges being present in the form of a

suspension which contains the isocyanate to be prepared, as a liquid, and carbamyl chlorides as a solid. Accordingly, the preferred embodiments described above for the process and the production plant apply to the novel use.

The use of film evaporators for working up reaction discharges from phosgenation reactors leads to the following advantages:

- The phosgene hold-up of the entire plant is permanently reduced, which is a substantial safety feature.
- A production plant can be designed so that the individual slim apparatuses are individually chambered and housing of the entire plant can be dispensed with.
- The capital costs are reduced, i.e. the cost efficiency increases.

The film evaporator has the following functions:

- Gentle vaporization of phosgene and HCl.
- Provision of flow substantially free of backmixing and with superposition of chemical reactions, in particular the decomposition of the carbamyl chloride into the desired product isocyanate and HCl.
- Introduction of heat of evaporation and heat of reaction.
- Substantial decrease in concentration of phosgene, HCl, suspended solids and dissolved reactants (from about 0.5% to 0.01 ppm).

Example:
Working-up of reaction discharges from phosgenation reactors

A stream III of the mixture of phosgene with a toluenediamine solution in monochlorobenzene having a mass flow rate of 0.111 kg/s was passed in liquid form from above into a first falling-film evaporator tube VI having an internal diameter of 1.5 inches and a length of 4 m, after the gas phase formed during mixing had been separated off. The stream had a temperature of T = 70°C. It contains 36% by mass of phosgene, 46% by mass of MCB, 17% by mass of carbamyl chloride and 1% by mass of HCl. At a pressure of 4.5 bar absolute (abs), a thermal power of about 8.5 kilowatt (kW) was transmitted via the casing to the falling-film evaporator tube. Vapor phase and liquid phase are passed countercurrently. The liquid phase was collected in a collector X and fed from above to a second falling-film evaporator tube VI having the same dimensions as the first falling-film evaporator tube. Here too, a thermal power of about 8.5 kW was transmitted at 4.5 bar (abs). Vapor phase and liquid

phase are passed countercurrently. The vapor phase of the second
falling-film evaporator tube was not passed through the first
falling-film evaporator tube. The liquid phase which was taken
off from the second falling-film evaporator tube contained, at a
5 temperature of T = 140°C, 8% by mass of phosgene, 66% by mass of
monochlorobenzene, 12% by mass of TDI and 13% by mass of carbamyl
chloride and was then let down to 2.5 bar through a valve VIII
into the container V. The liquid take-off from container V was
fed to a third falling-film evaporator tube VI having a length of
10 6 m and an internal diameter of 1.5 inches, for further
working-up. At a pressure of 2.5 bar (abs), a thermal power of
about 3.9 kW was transmitted to the falling-film evaporator tube.
Vapor phase and liquid phase were passed countercurrently. The
liquid phase taken off at the bottom was collected in the
15 collector X and fed from above to a fourth falling-film
evaporator tube VI having a length of 6 m and a diameter of
1.5 inches. At a pressure of 2.5 bar (abs), a thermal power of
about 3.9 kW was transmitted to the falling-film evaporator tube.
Vapor phase and liquid phase are passed countercurrently. The
20 vapor phase of the fourth falling-film evaporator tube is not
passed through the third falling-film evaporator tube. The liquid
discharge from the fourth falling-film evaporator tube still
contained, at a temperature of T = 160°C, 0.5% by mass of
phosgene, 68% by mass of MCB, 27% by mass of TDI and 3% by mass
25 of carbamyl chloride. The liquid discharge was first fed by the
conventional methods for distillative phosgene removal in a
distillation column and then further worked up by distillation to
give pure TDI. In the distillation column for phosgene removal,
the remaining carbamyl chloride also decomposed into TDI and HCl.
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